

PRODUCTION AND CHARACTERIZATION OF
CARBON DERIVED FROM COMPOUNDS OF INDENE (U)

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The advances in structural design associated with reactor, aerospace, and related technologies increase, in turn, demands for speciality forms of structural materials. One material that is finding special and strategic application in these areas is carbon. Increased use of carbon for other, more domestic applications is projected for the future. Interest in carbon as a fabrication material is prompted by the following: (1) high temperature heat resistance, (2) resistance to chemical attack, (3) constancy of properties with time, (4) the diverse properties which carbon can exhibit and the variety of product-type into which it can be made.

Since the properties exhibited by carbon can significantly vary, use of this material necessitates control of these properties. Our efforts involve two aspects of control: (1) reproducibility, with emphasis on use of synthetic raw materials as carbon precursors, (2) manipulative control, which would allow one to make carbon with specific and preselected properties by the appropriate choice of precursor and processing conditions. It is known that chemical, mechanical, electrical, and thermal properties of carbon, or parts fabricated from carbon, are greatly influenced by the carbon type; as is well known, carbon is generally classified in terms of amorphous, graphitic, and diamond structures. Properties associated with any given classification suggest a range of values. More specifically, properties of a graphitic carbon are a function of the degree of graphitization and certain other microstructural properties.

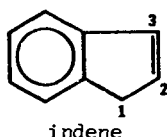
Have you considered the factors which contributed to the diverse properties exhibited by our natural deposits of carbon and carbonaceous products? Generalization will allow us to narrow the effects to two factors: (1) the nature of the organic matter from which the carbon was derived, (2) the conditions (pressure, temperature, time, etc.) under which the organic matter was converted to carbon. In our evaluation of carbon precursor materials, we have considered the same two factors. More specifically, we have attempted to correlate carbon properties with (1) the properties of the precursor material, with emphasis on effects attributed to molecular composition and structure, and (2) the processing conditions employed in converting the organic material into carbon, including the effect of temperatures up to 3000° C.

Some understanding of the relationships existing between carbon properties and precursor properties have evolved over the years. In general, organic materials which are or become infusible prior to pyrolysis do not tend to produce graphitic carbon. This type of material is characterized by thermosetting resins or highly crosslinked polymers. Thus, crystallinity seems to be dependent upon the ability of molecules to rearrange or reorient prior to pyrolysis, and such mobility necessitates an intermediate fluid or plastic state. Research efforts involving liquid crystal and mesophase studies represent attempts to correlate degree of orientation prior to pyrolysis with graphitic properties of derived carbon. Likewise, the planarity of polynuclear aromatic molecules will be a significant factor in determining the degree of graphitization of derived carbon. Molecules or molecular fragments that retain a nonplanar structure do not tend to graphitize. This seems reasonable in light of the planar, polynuclear structure that characterizes graphite. In addition to the inherent organic structure of the precursor materials, the presence of

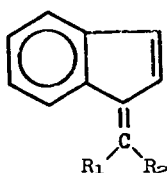
impurities such as sulfur and metallic compounds influence the graphitic properties of derived carbon.

Thus, precursor materials derived from natural sources will not be adequate for certain specialized applications since (1) they represent a complex mixture of organic structures whose composition varies with sources and refining methods, and (2) they frequently contain inorganic contaminants which vary in quantity and type with location of source.

This effort in the area of synthetic carbon precursors has included synthesis, polymerization, and carbonization studies. Much of the effort has been directed toward synthesis and evaluation of carbon precursor materials derived from indene (C_9H_8).



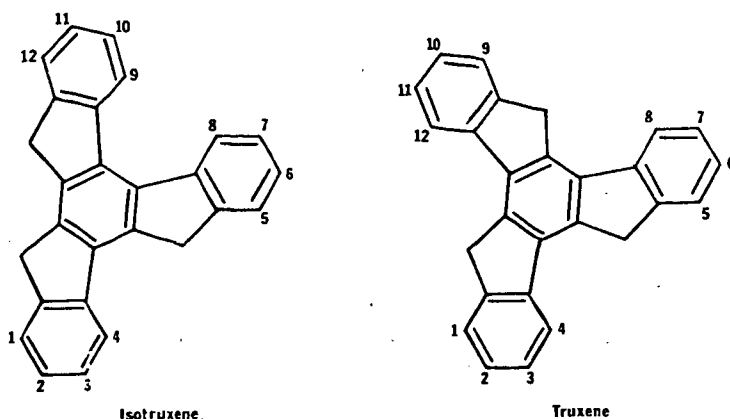
Included in the series were various indene derivatives incorporating the benzofulvene structures shown below.



	<u>R₁</u>	<u>R₂</u>	<u>Compound</u>
I	H	H	benzofulvene
II	CH ₃	CH ₃	dimethylbenzofulvene
III	H	C ₆ H ₅	benzylideneindene
IV	CH ₃	C ₆ H ₅	methylphenylbenzofulvene
V	C ₆ H ₅	C ₆ H ₅	diphenylbenzofulvene
VI	H	C ₆ H ₅ -CH=CH-	cinnamylideneindene

These compounds were synthesized by condensation reactions of indene with carbonyl compounds with the carbonyl component becoming an integral part of the benzofulvene structure.

Additional compounds that were derived from indene included α -truxene (truxene) and β -truxene (isotruxene), both of which are trimeric derivatives of indene. As shown by the structures below, the latter compounds are structural isomers.



The preparative procedures involve reactions of indene and carbonyl compounds in the presence of amine catalysts. Heretofore, only isomeric mixtures of these two compounds could be obtained by synthetic procedures involving autoclave conditions. However, procedures used in this study will allow production of either isomer under reflux conditions, and at the exclusion of the other. The specific isomer obtained will be a function of the carbonyl compound used in the formulation.

To lend emphasis to the correlations previously suggested between carbon properties, precursor properties, and processing conditions, truxene and isotraxene shall be discussed in detail. The influence of three factors on graphitizability of carbons shall be considered. These are the effect of (1) molecular structure, (2) metallic impurities, and (3) polymerization conditions.

Initially, structural effects will be considered. Though isomeric in structure, truxene yields a nongraphitic carbon while carbon derived from isotraxene tends to be graphitic. Two factors could contribute to the disoriented structure of truxene-derived carbon: (1) the planar structure that characterizes truxene molecules is apparently disrupted prior to pyrolysis and nonplanar intermediates are formed; (2) the fluid properties before and during pyrolysis were not conducive to orientation. As observed for other nongraphitizing materials, gases evolved during pyrolysis were entrapped, resulting in a cellular or foam-like carbon. Such gases tend to be freely evolved during pyrolysis of graphitizing materials, as was observed for isotraxene. These observations are indicative of the fluid properties existing during periods in which chemical change and structural realignments will be greatest. Lack of molecular mobility during these periods would tend to inhibit orientation. Attempts to control graphitic properties of carbons by blending graphitizing and nongraphitizing materials were considered. The materials must of necessity form homogeneous solutions and must yield a homogeneous carbon. For example, mixtures of isotraxene and truxene produce homogeneous carbons with properties that are dependent on composition. Data obtained by X-ray analysis of carbons derived from isotraxene and truxene-isotraxene mixtures are shown as a function of temperature in Table 1.

Table 1

CRYSTALLOGRAPHY STUDIES ON GRAPHITIC CARBONS FROM ISOMETRIC TRUXENES

Source of Carbon	Heat Treatment Temperature (°C)	d_{004} (Å)	C_0 (Å)	L_c (Å)	d_{110} (Å)	A_0 (Å)	L_0 (Å)
Isotruixene	2,800	1.6820	6.7280	314	1.2296	2.4592	259
Isotruixene	2,400	1.6845	6.7380	255	1.2299	2.4598	412
Isotruixene	2,000	1.7080	6.8320	126	1.2261	2.4522	135
Isotruixene-100	2,800	1.6317	6.7268	315	1.2294	2.4588	247
Isotruixene-truxene (75-25)	2,800	1.6914	6.7656	113	1.2300	2.4600	250
Isotruixene-truxene (75-25)	2,400	1.6946	6.7784	106	1.2290	2.4580	250

In one example of a study involving the effect of metallic impurities on graphitizability, samples of truxene-derived carbon containing induced metallic impurities were evaluated. Samples containing titanium carbide were fired to 2800° C, and were studied by X-ray analysis and photomicrography. Microstructural observation indicated large areas of graphitic carbon. As shown in Figure 1, X-ray data indicated an increased degree of graphitization as compared to the typically nongraphitic carbon derived from truxene. Other metals such as iron, nickel, chromium, or aluminum will also promote graphitization of typically nongraphitizing materials.

To show the effect that polymerization conditions can have on graphitizability, the oxidative polymerization of isotruixene will be considered. Without an oxidative cure, isotruixene yields an isotropic carbon that is not highly graphitic. After oxidative cure, X-ray analysis and microstructural examination indicate a more graphitic and a more anisotropic carbon. Changes in carbon properties with oxidative cure time are shown in Table 2.

In summary efforts to closely control properties of synthetic carbons must include close control on raw material properties and impurities, and conditions under which organic precursor materials are converted to carbon.

Table 2
EFFECT OF HEAT TREATMENT (300° C) IN OXYGEN ON THE PROPERTIES OF ISOTRUXENE AND ISOTRUXENE DERIVED CARBON(1)

Time (hrs)	Viscosity(2) (cp)	Oxygen Content(3) (%)	Melting Range (° C)	Apparent Monomer Content(4) (%)	Coke Yield at 1,000° C (%)	Carbon Properties After 3,000° C					
						d ₀₀₄ (Å)	g Factor	L _c (Å)	d ₁₁₀ (Å)	L _a (Å)	
Batch 10-82-69 (O ₂ Flow Rate, 40 cc/min)											
0	18.0	0.24	202 - 212	79.2	38.5	1.7010	0.422	120	1.2287	210	
24	22.0	0.43	78 - 187	81.2	42.5	1.6906	0.656	104	1.2299	289	
48	32.4	0.73	89 - 123	70.9	61.5	1.6914	0.633	112	1.2308	280	
72	56.8	1.10	93 - 142	64.5	63.5	1.6854	0.767	187	1.2307	419	
96	113.2	1.28	135 - 183	58.9	75.0	1.6860	0.756	187	1.2310	319	
125	427.2	1.43	182 - 196	57.6	78.0	1.6865	0.744	178	1.2304	361	
Batch 10-84-69 (O ₂ Flow Rate, 84 cc/min)											
0	17.2	0.31	201 - 209	82.7	45.0	1.7025	0.389	97	1.2292	200	
24	26.4	0.89	85 - 178	78.9	63.5	1.6900	0.667	102	1.2302	377	
48	61.2	1.29	123 - 163	64.4	61.5	1.6871	0.711	131	1.2303	362	
72	137.6	1.17	132 - 168	59.9	73.5	1.6845	0.789	200	1.2304	447	
91	627.2	1.09	184 - 222	58.5	83.5	1.6851	0.778	173	1.2303	424	
Batch 10-92-69 (O ₂ Flow Rate, 165 cc/min)											
0	18	0.24	208 - 216	69.0	26.0	1.7004	0.433	112	1.2292	206	
24	32.8	0.86	92 - 122	75.0	60.5	1.6882	0.711	122	1.2304	427	
48	108.0	1.45	143 - 178	56.0	77.0	1.6871	0.733	198	1.2307	591	
65 ⁽⁵⁾	-	0.62	> 300	(insoluble)	89.5	1.6882	0.711	129	1.2304	367	

(1) Isotruxene was heated at 300° C with constant agitation and with O₂ gas bubbling through molten material. Samples were removed periodically for evaluation.
 (2) Measured with Brookfield viscometer.
 (3) Determined by neutron activation.
 (4) Estimated from molecular distributions shown on GPC scans.
 (5) Material solidified after 65 hours of heating at 300° C, thus no viscosity was measured.

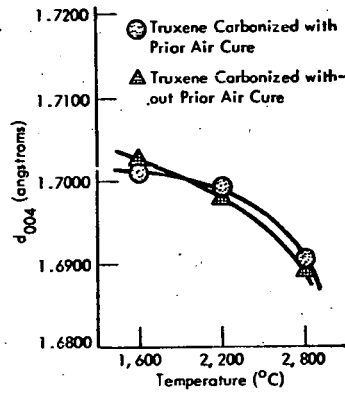


Figure 1. Correlation of Interlayer Spacing With Firing Temperature for Truxene-Derived Carbon Containing Titanium Carbide.